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WEAVING AND PYROLYSIS OF CONTINUOUS MULTIFILAMENT YARNS FROM PITCH PRECURSOR.

9 Final rept. Jan 76 - Sep 77,

10 M. K. / Towne

UNION CARBIDE CORPORATION
CARBON PRODUCTS DIVISION
PARMA TECHNICAL CENTER
PARMA, OHIO 44130

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This technical report has been reviewed and is approved for publication.

Stanley Schulman

Stanley Schulman
Project Engineer

FOR THE DIRECTOR

T. J. Reinhart, Jr.

T. J. Reinhart, Jr. Chief
Composite & Fibrous Materials Branch
Nonmetallic Materials Division

J. M. Kelble, Chief
Nonmetallic Materials Division

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Stabilized Carbon Fibers derived from pitch precursor were woven into fabrics of eight-harness satin, five-harness satin, and plain weave construction and subsequently pyrolyzed to produce six prototype fabrics for evaluation. Four of these fabrics utilized yarn of approximately 1350 denier and two of 2700 denier. Forty-eight yard samples of each fabric were delivered to AFML. Properties of the fabrics, as determined by Union Carbide Corp., are reported.

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20. ABSTRACT (cont'd.)

Two fabrics of eight-harness satif construction and one of five-harness satin, all utilizing the 1350 denier yarns, were selected for follow-on evaluation in the second phase of the program. Samples consisting of 120 yards each were submitted to AFML. Property data for these samples are reported.

Thermal conductivity and fiber density were found to be readily controlled by pyrolysis conditions and significant fabric strength was achieved under conditions producing desirably low thermal conductivity and density.

The low level of alkalinity desired was not achieved in the samples due to processing contamination and a transfer from a fugitive wrapping yarn used to facilitate weaving. The contamination was essentially eliminated in the second phase samples and a substantial improvement in the weavability of the fiber indicated that the wrapping yarn would not be necessary in future work.

Due to the improvement in the strength of the fabrics processed in the second phase of this program, it was found that a fabric produced under pyrolysis conditions to give even more favorable levels of thermal conductivity and density could have significant and perhaps staisfactory strength so a 25 yard sample of an eight-harness satin fabric pyrolyzed under these conditions was submitted to AFML for study.

PREFACE

The work reported herein was performed under the sponsorship of the Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433 on Contract No. F33615-76-C-5053. Mr. Stanley Schulman, Project Engineer, Composite & Fibrous Materials Branch, Nonmetallic Materials Division, AFML/MBC, provided technical direction.

The Contractor was Union Carbide Corporation, Carbon Products Division, 270 Park Avenue, New York, NY 10017. The work was performed at the Carbon Products Division's Parma Technical Center, P. O. Box 6116, Cleveland, OH 44101. Weaving service was provided by Fabric Development Inc., Quakertown, PA.

The Principal Investigator was Mr. M. K. Towne. Program assistance was provided by Dr. M. B. Dowell and Dr. H. F. Volk. Assistance in product evaluation was provided by Mr. J. Gibbons, Mr. J. Ziska, and Mrs. L. Satola. Extensive support was provided by the Analytical Department under Mrs. L. H. O'Connor and Mr. G. W. Jackson.

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SUMMARY

This report covers work performed between January 1976 and August 1977 on a program to develop a carbon fabric based on Union Carbide's pitch-based fiber, which would be suitable as a replacement for the currently used rayon-based fabric as a Missile Heatshield reinforcement. The work included the weaving, pyrolysis, and evaluation of six fabric variations concluding with the submission of 120 yard samples of three selected fabrics plus a 30 yard sample of a supplemental fabric at no additional cost to the Air Force. The fabric properties cover a broad range and should correlate with application test results to permit selection of an optimum fabric.

SECTION I

INTRODUCTION

The objective of the program described in this report was to develop woven fabrics made from continuous multifilament pitch precursor yarn which would be suitable as reinforcements in resin matrix heatshields.

Current Air Force missile systems utilize in their heatshields carbon fabrics made by the pyrolysis of viscose rayon fabrics. The decline in recent years in the industrial and commercial requirements for rayon fabric and the subsequent production termination by the historical producers has cast doubt on the continued availability of suitable rayon materials into the long-term future. Consequently, it has become necessary to investigate other precursor materials as possible replacements for the rayon in the heatshield before the need becomes critical.

Carbon fabrics based on pitch precursor yarn which were first introduced commercially in 1975 by Union Carbide exhibited many of the attributes desired for a heatshield reinforcement and thus demonstrated the potential of a pitch precursor fabric as a replacement for the rayon-based material. The commercially introduced fabrics, however, did exhibit several drawbacks which detracted from their suitability as heatshield materials. These were high density, high thermal conductivity, heavy fabric construction, and a relatively high level of alkaline impurities. It was consequently the goal of this program to tailor a fabric to the specific heatshield requirements by eliminating or minimizing the undesirable characteristics.

The pitch-based fibers, as produced by Union Carbide, are in the "as spun" condition highly oriented and possess a high carbon content. It is consequently relatively easy to achieve during subsequent thermal processing high densities and high degrees of anisotropy leading to high thermal conductivity in the longitudinal direction. In the development of the commercial fabrics, thermal processing cycles had been selected to optimize certain mechanical properties of the fibers with little consideration being given to density and thermal conductivity; thus a compromise in these mechanical properties, particularly tensile strength, to obtain the desired lower density and thermal conductivity was indicated at the conception of this program.

Also in the development of the commercial fabrics, weaving cost had been a major consideration. To minimize this cost a relatively heavy 2250 denier yarn had been used which consisted of essentially three plies of "as-spun" yarn. It was also very difficult at that stage of the pitch fiber development to weave the carbonized pitch fiber at economical speeds so in consideration of the ease with which the pitch fibers could be carbonized, the commercial fabrics had been woven using a partially processed fiber which exhibited good elongation and final carbonization had been accomplished on the fabric itself. As an additional aid in increasing weaving speeds, the intermediate yarns were either twisted or served with a double opposed helical wrap of a 50 denier rayon yarn which was subsequently burned off in the final carbonization step. The resulting "economic" fabric for commercial use was consequently quite a bit heavier than that desired for heatshield applications, so a weaving program oriented toward lighter weight stable fabrics, perhaps utilizing lower denier yarns, was required.

The alkaline impurities in the commercial pitch cloth consisted primarily of sodium with lesser amounts of calcium and potassium. The sodium was not considered an inherent impurity in the pitch fiber but a known additive during processing. Since Union Carbide at the time of the inception of this program was already planning to eliminate the sodium in a separate effort, the alkalinity was not considered to be a significant impediment to the development of a suitable heatshield fabric.

Property goals for the fabric to be developed in this program were derived primarily from the current rayon-based fabric where pertinent. These are shown in Table 1.

The program was to consist of two phases. In the first phase, six prototype fabrics were to be constructed representative of current rayon fabric constructions including at least one eight-harness satin fabric. Pyrolysis schedules were to be developed for these fabrics to achieve properties consistent with the requirements of heatshield reinforcements and sample quantities of 25 yards (later increased to 40 yards) of each fabric delivered to AFML/MBC for evaluation. In the second phase of the program, three fabrics selected from the six were to be produced in lengths suitable for evaluation of reproducibility and 100 yard samples delivered to AFML/MBC.

TABLE 1

FABRIC PROPERTY GOALS

Breaking Strength	lb/inch width	
Warp Direction		20 minimum
Fill Direction		20 minimum
Fabric Thickness, inches		0.017 - 0.021
Carbon Assay, wt. %		94 minimum
Specific Gravity at 25°C		1.90 maximum
Thermal Conductivity, longitudinal in fiber		$\leq$ 0.01 Cal/cm sec °C
Ash Content, wt. %		0.5 maximum
Alkalinity, pph		
Sodium		70 maximum
Total (Na, Ca, K, Mg, Li)		150 maximum

SECTION II

FABRIC WEAVING AND PYROLYSIS - PHASE I

At the start of this program the Air Force requested that the spinning of the fiber to be used for the six prototype fabrics be postponed until Union Carbide was successful in eliminating the sodium contamination. This proved to be much more of a problem than had been anticipated and essentially delayed the program for five months. The sodium had been introduced in the spinning size used in the process and elimination of the sodium-containing ingredient caused material handling problems which resulted in considerable damage being done to the fibers. Before that problem had been solved to the point where handleable fibers could be produced, Union Carbide made a basic change in the denier of the filaments being produced for its commercial products, and for consistency, that change was adopted for the fibers to be made for this program also. The result was that the denier for the basic 720 filament single ply increased from about 725 to about 1360.

While waiting for the sodium problem to be resolved, pyrolysis studies were made with strands of the new high denier fiber in the production furnace to be used for the final carbonization of the fabrics. The electrical resistivity of the fibers was measured as a guage of thermal conductivity according to the relationship given in I. Kalnin's report, AFML-TR-73-191, which is shown in Figure 1. That relationship was assumed to hold for pitch precursor fibers based on a data point obtained by AFML on yarn taken from Union Carbide's standard commercial pitch fabric, grade VC-0139.

Six thermal processing cycles were used to process single and three ply yarns for which density, electrical resistivity, tensile strength, and modulus were then measured. These properties are shown in Table 2 and the electrical resistivities are also shown in Figure 1.

The tensile results in the following table were obtained on strands and were not considered too reliable as it was very difficult to uniformly tension the individual filaments. The higher strength for the Cycle B yarns relative to Cycle A were not consistent with other work so single filament tests were also run and shown in parentheses. Single ply yarns of later fiber lots were also processed at A and B conditions as a check on the first results and these are shown at the bottom of the table and confirm the higher strength for Cycle A.

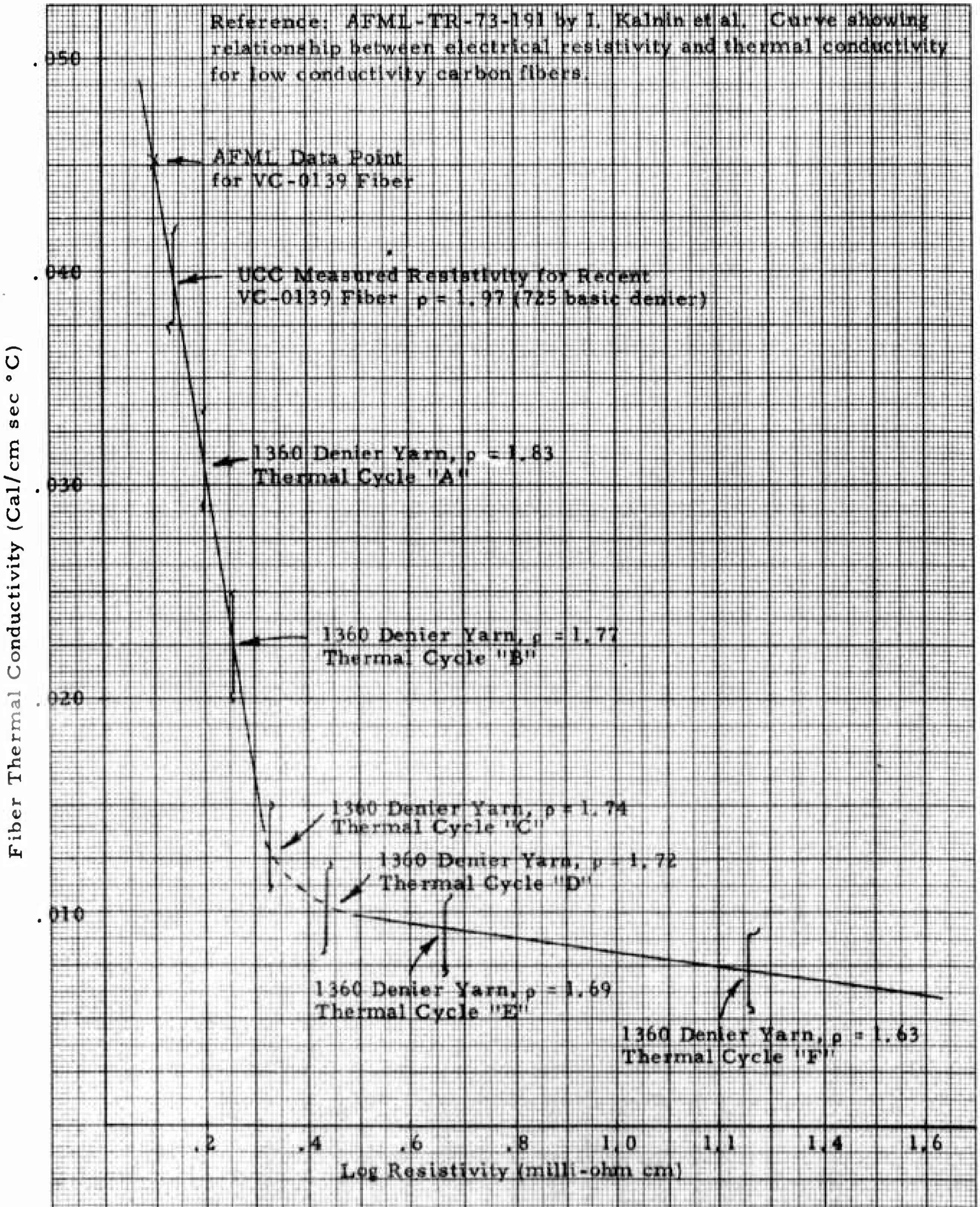

Figure 1. Thermal Conductivities of Pitch Fibers Processed Under Various Thermal Cycles, Estimated from Electrical Resistivities

TABLE 2

RESULTS OF THERMAL PROCESSING TRIALS

Thermal Cycle	Density g/cc	Elec. Resistivity milli-ohm-cm	Tensile Str. Ksi	Modulus Msi
A - single ply	1.83	1.58	82.6 (SF=109)	17.4 (SF=18.3)
A - three ply	1.84	1.53	88.2	17.3
B - single ply	1.77	1.78	105.3 (SF=105)	16.2 (SF=17.3)
B - three ply	1.77	1.81	107.5	17.1
C - single ply	1.74	2.16	99.8	16.4
C - three ply	1.74	2.13	79.1	15.1
D - single ply	1.71	2.73	96.3	14.9
D - three ply	1.72	2.78	72.3	14.6
E - single ply	1.71	4.75	75.1	12.3
E - three ply	1.68	5.00	80.0	12.4
F - single ply	1.64	18.2	58.1	9.7
F - three ply	1.62	21.3	53.5	10.0
Yarn from VC-0139	1.97	1.37		
A - single ply (new lot)	1.82	1.64	98.3 (SF=141)	17.1 (SF=18.6)
B - single ply (new lot)	1.78	1.80	91.2 (SF=131)	16.5 (SF=16.5)

Upon examination of the results in Table 2 and Figure 1 it was decided, in conjunction with AFML personnel, to introduce the thermal cycle as a variable in the six prototype fabrics. Three weave styles, 8 harness satin, 5 harness satin, and plain weave were considered representative of current rayon-based fabrics and in consideration of the potential economic advantages, two ply as well as single ply yarns were included to make up the six fabrics. The six prototype fabrics thus became as follows:

# 1	24x23	eight-harness satin	single ply	Thermal Cycle B
# 2	24x23	eight-harness satin	single ply	Thermal Cycle C
# 3	14x14	eight-harness satin	two ply	Thermal Cycle C
# 4	22x21	five-harness satin	single ply	Thermal Cycle C
# 5	23x18	plain weave	single ply	Thermal Cycle D
# 6	13x10	plain weave	two ply	Thermal Cycle B

Thermal Cycle A was not included as it appeared to offer no advantage over Cycle B; Cycles E and F, although offering better densities and thermal conductivities, were considered to produce tensile strengths too low to be handleable as fabrics.

The six fabrics were to be woven by Fabric Development Inc. in 22 inch widths on standard shuttle looms. The 22 inch width was selected to permit the fabric to pass through a 24 inch wide carbonizing furnace at Union Carbide's Greenville, SC plant.

Production of the fiber for the program was finally authorized after samples of the as-spun fiber gave theffollowing analysis:

Na	K	Ca	Mg	Li
25.6 ppm	7.7 ppm	100 ppm	4.1 ppm	0.01 ppm

The high level of Ca was considered to be a random raw material variable and although undesirable at that point its removal was not a simple matter and would be addressed by a seaparate program that could not be accomplished for several months.

The fibers, particularly the single ply material, was still rather difficult to handle so the wrapping approach was selected to facilitate weaving. A double wrap of 50 denier "Bemberg" rayon was applied to the yarn. The rayon had been analyzed for impurities and found to contain about 700 ppm sodium. Upon carbonization the rayon yarn becomes a light dust on the cloth surface most of which is removed during subsequent handling and clean-up of the fabric. It was calculated that the maximum amount of sodium which could be introduced from the wrap would be 50 ppm for the single ply and 25 ppm for the two-ply yarns.

The weaving proceeded with no significant problems although the wrapping operation was slowed by some difficulty in removing the single ply yarn from the supply packages. The weaving was accomplished in a partitioned off area at Fabric Development Inc.'s plant and the operators wore gloves to minimize contamination.

The fabrics were carbonized according to the previously determined thermal cycles during September and October 1976 and all appeared to be in good condition. The fabrics had shrunk slightly as had been expected to about 20 inches in width and to compensate for the reduced width 48 yard samples of each fabric were submitted to AFML/MBC.

The results of the tests conducted on the fabrics by Union Carbide are shown in Table 3.

Fiber strength and moduli as shown in the table were obtained on 19.8 mm filaments which retained some residual crimp which made measurements difficult so these numbers, particularly the moduli, may be somewhat low. An anomaly exists in the density and resistivity measurements on Fabric #4 in that the values indicate that Cycle B conditions were used. However, a recheck of the furnace conditions at the time that fabric was processed indicate that Cycle C was indeed used. The surface area measurements are also somewhat confusing in that Cycle D, Fabric #5, was expected to show the highest area and indeed shows the lowest.

TABLE 3

PROTOTYPE FABRIC PROPERTIES

Fabric Designation Thermal Cycle Weave Style	AFML #1 VC-0142-1 Cycle B 8-harness satin Single Ply	AFML #2 VC-0142-2 Cycle C 8-harness satin Single Ply	AFML #3 VC-0143-2 Cycle C 8-harness satin Two Ply	AFML #4 VC-0144-2 Cycle C 5-harness satin Single Ply	AFML #5 VC-0145-3 Cycle D Plain Weave Single Ply	AFML #6 VC-0146-1 Cycle B Plain Weave Two Ply
Yarn Count/inch Warp x Fill	26 x 24	26 x 24	15 1/2 x 14 1/2	23 x 22	25 x 21	14 x 11
Thickness, inch	0.020	0.020	0.024	0.018	0.020	0.022
Weight, oz/yd^2	9.7	9.7	11.6	8.9	9.2	9.6
Fabric ρ g/cc	1.81	1.75	1.74	1.80	1.70	1.80
Fabric Strength lb/in, W/F	19/13	18/19	9/13	15/42	21/13	10/7
Resistivity, ohm-cm x 10^{-4}	18.1	25.2	23.5	18.0	29.0	17.8
Filament Strength (19.8 mm), Ksi	84.1	84.0	75.1	93.3	34.4	63.9
Filament Modulus (19.8 mm), Msi	12.0	12.7	14.3	14.8	8.8	14.8
Surface Area m^2/gm (Kr)	1.24	1.25	1.05	1.22	1.00	1.27
Carbon Assay %	97.8 ± 0.8	98.1 ± 0.8	97.6 ± 0.8	97.5 ± 0.8	95.8 ± 0.8	98.0 ± 0.8

	AFML #1			AFML #2			AFML #3			AFML #4			AFML #5			AFML #6		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Impurity Analysis Ash %	0.16	0.18	0.17	0.17	0.15	0.19	0.09	0.09	0.12	0.11	0.11	0.10	0.18	0.18	0.13	0.11	0.10	0.10
Alkalinity, ppm																		
Na	190	390	240	350	320	430	150	160	160	190	360	140	260	120	200	140	110	130
K		15.5			15.4			12.0			26.8			8.7			12.2	
Ca	140	170	150	160	150	160		110			320		260	100	160	150	140	140
Mg		4.4			8.9			6.2			12.3			8.3			8.3	
Li		0.02			0.03			0.05			0.16			0.04			0.04	
Total Alk., avg.		446			548			284			589			383			291	

The real surprise in the data appeared in the impurity values. Both the high levels and the variability in the sodium and in some cases the calcium were not at all understandable. Samples A, B, and C were not duplicate samples but were obtained so that A and B contained the same fill yarns but different warp yarns. Sample C contained warp from a third area and was taken far enough from A and B so that a different package of fill yarn was likely. The analyses were made using the Atomic Adsoprtion technique and the average sample size was over 15 grams so it is very unlikely that handling contamination could significantly affect the results. At the same time as the yarn was made for this program, some similar yarn was woven without any wrapping and the Na levels on three samples of that material ranged from 130 ppm to 170 ppm, which confirms that the contamination existed at least to some degree before the wrapping.

Unfortunately, samples of yarn were not taken throughout the process so it was impossible to trace the contamination to a particular point in the process. This would have to be done before starting on the second phase of the program.

In addition to the evaluation made on the fabric itself and since the strength and modulus values were so questionable, epoxy composite plates were made from each fabric and the mechanical properties obtained on these places are shown in Table 4.

TABLE 4

COMPOSITE PROPERTIES (EPOXY MATRIX)*
PROTOTYPE FABRICS

Fabric	VC-0142-1 (AFML #1)	VC-0142-2 (AFML #2)	VC-0143-2 (AFML #3)	VC-0144-2 (AFML #4)	VC-0145-3 (AFML #5)	VC-0146-1 (AFML #6)
Tensile Str., Ksi	22.3	22.9	16.7	23.7	15.4	19.9
Tensile Mod., Msi	4.8	4.5	4.1	4.9	3.6	4.6
Compress. Str., Ksi	44.7	35.1	35.3	34.8	25.2	21.5
Flex. Str., Ksi (Warp)	34.4	32.9	28.2	31.2	21.6	25.6
Short Beam Shear, Ksi	5.2	5.2	4.5	5.0	4.0	5.0

* All properties except shear normalized to 55% Fiber Volume.

SECTION III

FABRIC WEAVING AND PYROLYSIS - PHASE II

Upon evaluation of data collected by Union Carbide and AFML on the fabrics, and by Avco on phenolic composites made from the fabrics under another AFML contract, the three fabrics selected for the second phase of the program were the two eight-harness satin, single ply fabrics, VC-0142-1 and VC-0142-2, and the five-harness satin fabric, VC-0144-2. The two ply fabrics were considered to be substantially poorer in quality than the single ply materials.

Prior to starting production of the fiber for these fabrics the production line was completely cleaned and a trial run made with samples being taken at every possible point in the process. Sodium levels ranged from 12-29 ppm. Authorization was given to proceed with the production but again samples were taken at each point in the process after the first day of operation. By the time these samples were analyzed, the production run was complete and the material shipped to the weaver. Analysis showed that every sample taken after the application of the weaving size contained a high variable amount of sodium ranging from 65 to 185 ppm although fresh weaving size contained less than 1 ppm. Subsequent samples of the material sent to the weaver were also found to be variable. The program was stopped at this point and the material returned to the Greenville plant by the weaver.

Analysis of the problem in the sizing operation indicated that a buildup of contaminant was occurring in the recirculating system and that after cleaning and fresh sizing addition, low values were obtained. Modifications were, therefore, made to the sizing system to prevent recirculation from the parts of the system which were believed to be the source of the contamination. During subsequent remake of the fibers for this program, samples of the sized fibers were taken every few hours and sent to the R. S. Noonan Laboratory in Greenville for sodium analysis. Their values of ten samples throughout the run ranged from less than 1 ppm to 18 ppm. Cross-check analyses on two of the samples at Parma were in good agreement in one case, 15 ppm vs 13.5 ppm, but poor agreement in the other, 1 ppm vs 27 ppm. However, since 30 ppm had been established as the maximum permissible level, all of the material was shipped to the weaver.

It was obvious throughout the spinning of these fibers, both the good material and that which became contaminated, that their handling quality was much superior to those fibers produced for the six prototype fabrics and there was no question that this material could be woven with a slight twist and no wrapping. Some of the material, in fact, was used as fill yarn in an Iwer loom without any twist or wrap and performed very well. However, since the prototype fabrics had been woven with the rayon wrap, the same procedure was used in this phase of the program. The Bemberg rayon was again analyzed for sodium and found to be in the same 700 ppm range as previously.

The weaving and the thermal processing were accomplished routinely and, as before, since the fabric width was about 21 inches, 120 yard samples were supplied to AFML/MBC. For the evaluation of these fabrics, samples were taken at three places for each fabric and each location was at least 50 yards from any other sample in order to gain a measure of reproducibility.

The results of the fabric evaluation and the corresponding epoxy composite data are given in Tables 5 and 6 , respectively. The general improvement in these fabrics compared to the prototype samples is illustrated by the fabric pull strength figures even though it is not obvious in the single filament test due to the residual crimp in the test filaments. Electrical resistivities were somewhat lower than the corresponding prototype fabrics, however, this also may be indicative of an improvement in the fiber and could be adjusted by a slight change in thermal processing during a longer production run.

A real anomaly occurred in the surface area measurements where only one sample per thermal cycle was tested. None of the samples checked with the prototype samples. Part of the discrepancy may be due to the fact that nitrogen was used instead of krypton, however, an effort was first made to use krypton on these samples and the area was found to be too great. Further study of this problem is warranted but time did not permit it to be addressed in this program.

TABLE 5

SELECTED FABRIC PROPERTIES

Fabric No. / Style	VC-0142-1 (AFML #1) Thermal Cycle "B" 8-harness satin			VC-0142-2 (AFML #2) Thermal Cycle "C" 8-harness satin			VC-0144-2 (AFML #4) Thermal Cycle "C" 5-harness satin		
	Sample I	Sample II	Sample III	Sample I	Sample II	Sample III	Sample I	Sample II	Sample III
Yarn Count/inch Warp x Fill	25 x 24 1/2	24 1/2 x 24	26 x 24	25 x 26	25 1/2 x 25	25 1/2 x 24 1/2	22 1/2 x 23 1/2	23 x 22 1/2	21 1/2 x 22
Thickness, inch	0.018	0.018	0.018	0.019	0.018	0.0175	0.018	0.0175	0.017
Weight, oz/yd^2	10.0	9.9	10.1	10.2	10.0	10.0	9.3	9.3	9.2
Fabric Density g/cc	1.82	1.81	1.81	1.77	1.78	1.75	1.77	1.77	1.75
Fabric Strength lb/in, W/F	48.6/53.1	48.8/35.8	52.0/38.6	39.7/44.6	52.3/38.7	51.0/32.5	27.4/32.6	38.8/37.5	40.2/39.6
Resistivity, ohm-cm x 10^{-4}	16.4	15.5	16.6	19.8	19.7	19.9	19.5	20.4	20.1
Filament Strength (19.8 mm), Ksi	101.2	77.7	87.4	68.4	81.6	82.6	77.9	75.1	68.1
Filament Modulus (19.8 mm), Msi	14.9	14.9	14.9	13.9	14.6	14.2	13.9	13.8	13.2
Surface Area m^2/gm (N_2)	----	22.8	----	----	----	3.6	15.1	----	----
Carbon Assay %	97.6 ± 1.1	----	98.1 ± 1.1	96.8 ± 1.1	96.9 ± 1.1	----	----	97.0 ± 1.1	96.6 ± 1.1
Impurity Analysis	A B C	A B C	A B C	A B C	A B C	A B C	A B C	A B C	A B C
Ash %	0.19 0.18 0.21	0.23 0.20 0.19	0.19 0.18 0.18	0.21 0.22 0.21	0.20 0.20 0.19	0.18 0.18 0.17	0.19 0.17 0.17	0.21 0.22 0.20	0.15 0.18 0.20
Alkalinity, ppm									
Na	134 129 159	179 161 148	134 129 114	154 184 147	148 136 85	187 173 150	153 125 148	179 169 169	110 132 128
K	9.1 9.6 8.2	13.1 12.4 10.8	11.5 9.5 9.1	10.1 10.4 17.6	10.0 10.9 7.4	13.4 14.0 10.4	17.0 12.9 13.4	14.3 17.5 18.0	11.8 8.7 9.5
Ca	4.2 4.6 5.9	5.5 5.3 5.0	4.6 3.7 4.9	3.5 3.9 3.8	5.7 3.3 4.2	5.3 5.6 5.3	5.4 4.8 4.9	5.5 5.6 6.0	5.4 5.6 5.5
Mg	3.8 4.0 4.4	4.2 4.1 4.0	3.8 3.0 3.4	4.3 4.4 5.8	4.8 4.4 3.3	4.1 4.1 4.5	4.8 3.7 4.2	4.7 4.8 5.6	3.1 3.3 4.1
Li	0.1 0.1 0.1	0.1 0.1 0.1	0.1 0.1 0.1	0.1 0.1 0.1	0.1 0.1 0.1	0.1 0.1 0.1	0.1 0.1 0.1	0.1 0.1 0.1	0.1 0.1 0.1
Total Alk., avg.	151 147 178	202 183 168	154 145 132	172 203 174	169 155 100	210 198 170	180 146 171	204 197 199	130 150 147

TABLE 6

COMPOSITE PROPERTIES (EPOXY MATRIX)*
THREE SELECTED FABRICS

Fabric	VC-0142-1 (AFML #1)			VC-0142-2 (AFML #2)			VC-0144-2 (AFML #4)		
Sample	#1	#2	#3	#1	#2	#3	#1	#2	#3
Tensile Str., Ksi	27.9	25.7	25.6	23.8	20.3	23.2	18.1	20.9	22.4
Tensile Mod., Msi	4.6	4.6	4.5	4.4	4.6	4.3	4.3	4.6	4.3
Compress. Str., Ksi	42.4	47.7	37.2	36.8	38.9	30.8	29.2	29.5	31.9
Flex. Str., Ksi (Warp)	36.2	37.8	30.1	30.1	32.9	28.4	25.8	32.7	30.9
Short Beam Shear, Ksi	5.2	5.1	4.9	4.4	4.7	4.6	4.5	4.7	5.1

* All properties except shear normalized to 55% Fiber Volume.

Again, despite all the precautions, the sodium contamination level is higher than expected although not as variable as in the prototype fabrics. Contamination during weaving was ruled out as a cause by some other work which indicated that at the 10 ppm sodium level an insignificant increase in sodium occurred through weaving and carbonization even when no special precautions were taken. Two other possibilities seemed to exist: that the material as shipped to the weaver was higher than measured by the Noonan Labs or that more contaminant is transferred from the wrap yarn than was believed possible by calculations from the relative amount of pitch to rayon in the wrapped yarn and the 700 ppm level in the rayon. To check the first possibility, four other samples from the ten checked by Noonan Labs were rechecked by Parma. The levels were 13, 18, 39, and 73 ppm so two of the ten samples are known to be above the acceptable level but still not high enough to have caused the high numbers obtained. As to the second possibility re-examination of the contaminant levels in the prototype fabrics in Table III does show a significantly higher sodium level in the fabrics from single ply yarn than in the fabrics made from two ply yarn. The average of the sodium levels in the single ply materials is 266 compared to 141 for the two ply materials. This is a substantially greater difference than the 25 ppm difference that theoretically would have occurred if all the contaminant from the rayon wrap remained in the fiber after carbonization, and if 700 ppm were the true value in the rayon. In view of the improvement in the weavability of the fiber it appears the best solution to this problem would be to circumvent it altogether and use a light twist in the yarn and not apply the wrapping yarn at all.

SECTION IV

SUPPLEMENTAL FABRIC

At the time the six prototype fabrics were selected, the thermal cycles chosen were based on the results of the single and three ply yarns which were processed under those same conditions. Cycles E and F, which produced material with the best density and resistivity, were excluded because the yarn appeared to be too weak and it was estimated that fabrics containing yarns of that strength would not be sufficiently handleable. In view of the apparent excellent handleability of Fabric #5 processed at Cycle D and some subsequent fabric processing apart from this program at cycles similar to E and F, it was decided to process a small swatch of fabric at Cycle F to evaluate its handleability. The resulting fabric was not as strong as that produced by Cycles B and C but it was difficult to conclude that it was not handleable.

Consequently, on the possibility that a superior fabric for the heat-shield application might have been overlooked, Union Carbide offered, at no additional cost, an evaluation quantity of the eight-harness satin weave fabric processed at Cycle F conditions. A 30 yard sample was subsequently submitted along with the 120 yard samples in Phase II of the three selected fabrics. The data obtained by Union Carbide on this fabric is presented in Table 7. Compared to the pull strengths of the fabrics in Table 5, this one was relatively weak although it did not seem to present any handling difficulties. The resistivity is actually greater than that obtained with Cycle F previously in the yarn samples, and according to Kalnin's curve in Figure A equates to a thermal conductivity of 0.0075 cal/cm sec °C. It is probable, however, that resistivity in that range cannot be controlled by thermal processing quite as closely as at lower levels. The overall properties, while not completely consistent with the goals in Table 1, may, in fact, be quite suitable for a heatshield reinforcement.

TABLE 7

PROPERTIES OF SUPPLEMENTAL FABRIC

Fabric Designation	VC-0142-5		
Thermal Cycle	Cycle "F"		
Style	8-harness satin, single ply		
Yarn Count per inch Warp x Fill	24 x 24		
Thickness, inch	0.020		
Weight, oz/yd^2	10.8		
Fabric Density, g/cc	1.62		
Fabric Strength, lb/inch Warp/Fill	10.9/8.9		
Resistivity, ohm-cm x 10^{-4}	356		
Filament Strength (19.8 mm), Ksi	48.0		
Filament Modulus (19.8 mm), Msi	8.6		
Surface Area, m^2/gm	39.9		
Carbon Assay %	91.0 ± 1.0		
Impurity Analysis	**A**	**B**	**C**
Ash %	**0.16**	**0.16**	**0.18**
Alkalinity, ppm			
Na	**103**	**121**	**135**
K	**4.5**	**6.8**	**7.2**
Ca	**4.7**	**4.7**	**5.9**
Mg	**3.3**	**3.7**	**4.6**
Li	**0.1**	**0.1**	**0.1**
Total Alkalinity	**116**	**136**	**153**

SECTION V

CONCLUSIONS

Although this program was plagued by many problems due primarily to the fact that it was conducted during a period of developing technology in Union Carbide's pitch fiber program, some very positive results were obtained. The three fabrics submitted in Phase II all appeared to be very suitable physically for a heatshield application. The dramatic improvement in the weavability of the fiber from Phase I to Phase II certainly indicates that the wrap yarn, which was obviously the cause of some contamination, could be eliminated in any future requirement for high purity fabric. With additional modification in the equipment where the weaving size is applied prior to packaging, there is no question that sodium levels can be kept well within requirements. The eight-harness satin fabrics from Cycle B to Cycle F certainly bracket a range of properties from which an optimum fabric could now be selected based on a correlation with composite properties pertinent to the heatshield application.

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